

Patent
Case 1731

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

PATENT APPLICATION: Joachim E. Klee et al

Serial No. PRIOR Art Unit: 1712

Filed: HEREWITH PRIOR Examiner: M. Moore

For: POLYMERIZABLE COMPOUNDS AND COMPOSITIONS

The Commissioner of Patents and Trademarks
Washington, D.C. 20231

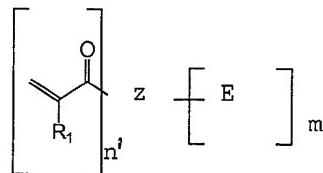
PRELIMINARY AMENDMENT

In the Claims

Cancel claims 1-23.

Please add claims 24-45 as follows [clean copy]:

--24. An esterified macromonomer obtainable by esterification of at least a portion of the -OH groups of a macromonomer having at least one terminal double bond with at least one derivative of an inorganic or organic acid whereby pendant groups are introduced exhibiting at least one acid moiety selected from the group of consisting of -COOH, -PO₃H₂, -SO₃H, -BO₂H and salts thereof, whereby the esterified macromonomer is within the scope of the general formula:



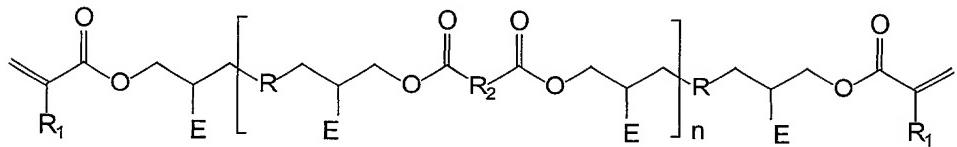
wherein Z is an organic moiety,

R₁ is hydrogen or a substituted or unsubstituted alkyl having from 1 to 12 carbon atoms, oxyalkyl having from 1 to 12 carbon atoms, alkenyl having from 2 to 12 carbon atoms, cycloalkyl having from 5 to 12 carbon atoms, aryl having from 6 to 12 carbon atoms or aralkyl having from 7 to 12 carbon atoms,

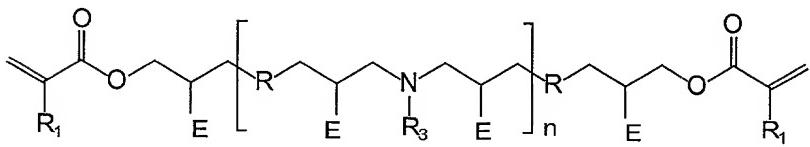
each E independently is a hydroxyl group, an organic or inorganic ester moiety and at least one E is an organic or inorganic ester moiety,

n' and m each independently is an integer from 2 to 12.

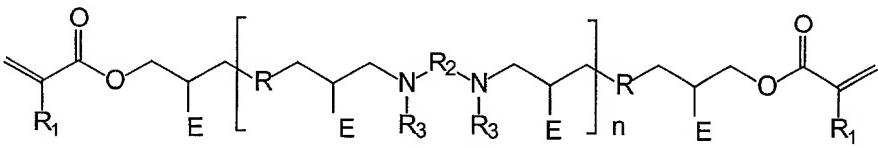
25. The esterified macromonomer of claim 24 wherein said esterified macromonomer is within the scope at least one of formulas **M-1** to **M-12**:



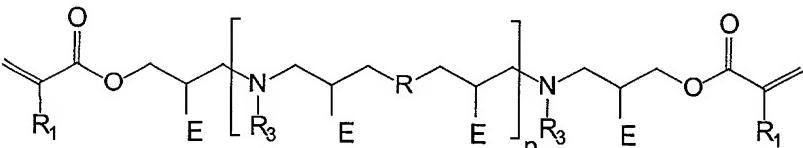
M-1



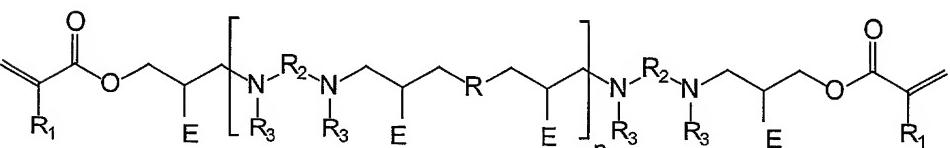
M-2



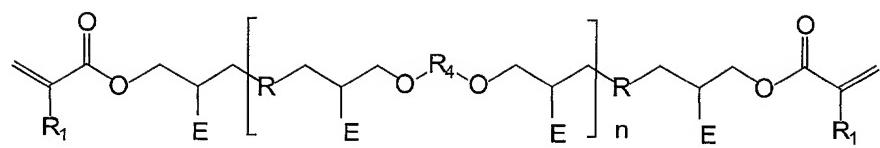
M-3



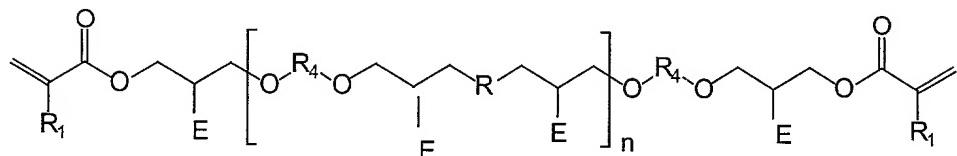
M-4



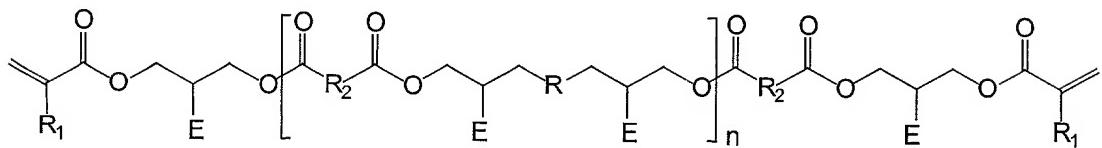
M-5



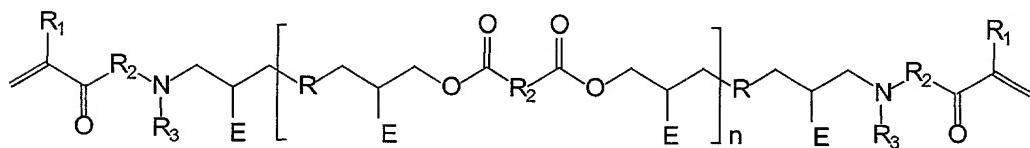
M-6



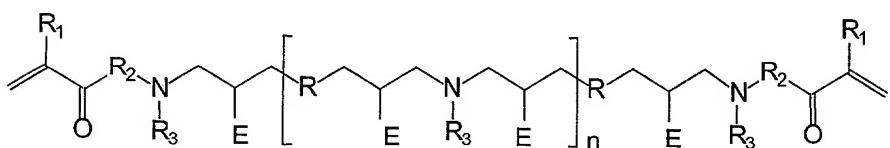
M-7



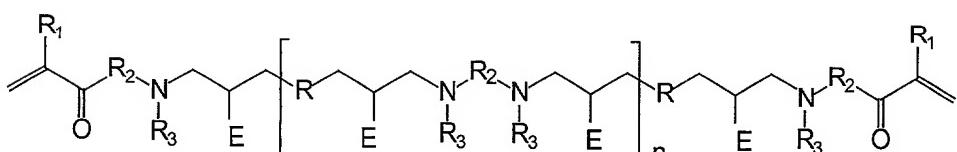
M-8



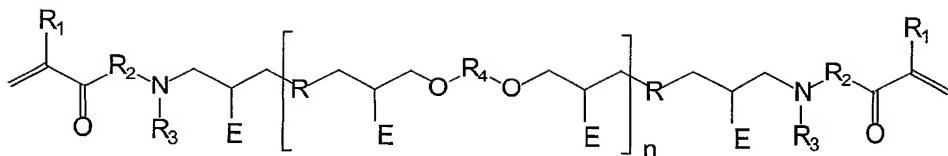
M-9



M-10



M-11



M-12

wherein

R is a diether containing moiety , or diester containing moiety or tertiary
amine containing moiety,

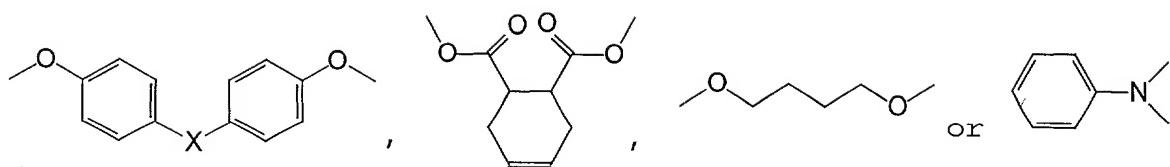
R₂ is a difunctional substituted or unsubstituted alkyl group having from 1
to 12 carbon atoms, alkenyl group having from 2 to 12 carbon atoms,
cycloalkyl having from 5 to 12 carbon atoms, aryl having from 6 to 12
carbon atoms or aralkyl having from 7 to 12 carbon atoms,

R₃ is hydrogen or a substituted or unsubstituted alkyl group having from 1
to 12 carbon atoms, alkenyl group having from 2 to 12 carbon atoms,
cycloalkyl having from 5 to 12 carbon atoms, aryl having from 6 to 12
carbon atoms or aralkyl having from 7 to 12 carbon atoms,

R₄ is a substituted or unsubstituted aryl having from 6 to 12 carbon atoms,

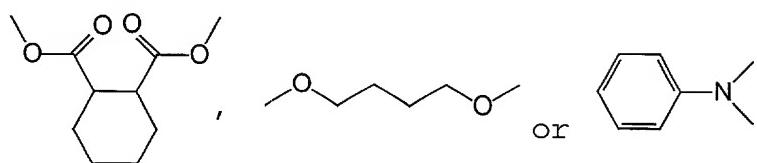
and n is an integers of at least 1.

26. The esterified macromonomer of claim 25 wherein R is within the
scope of the general formula:

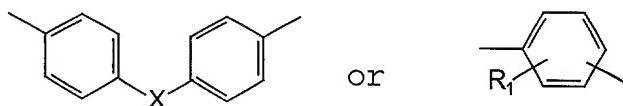


wherein X is C(CH₃)₂, -CH₂-, -O-, -S-, -CO-, or -SO₂-.

27. The esterified macromonomer of claim 25 wherein R is



28. The esterified macromonomer of claim 25 wherein R₄ is within the scope of at least one of the general formulas:



wherein X is C(CH₃)₂, -CH₂-, -O-, -S-, -CO- or -SO₂-.

29. The esterified macromonomer of claim 25 wherein at least one E comprises a carboxyl group.

30. The esterified macromonomer of claim 24 wherein E is derived from succinic acid anhydride, maleic acid anhydride, dichloro maleic acid anhydride, dimethyl maleic acid anhydride, malonic acid anhydride, aconit acid anhydride, adipic acid anhydride, 3,3-tetramethylen glutaric acid anhydride, cyclohexen-1,2 acid anhydride, nadinic acid anhydride, phthalic acid anhydride, trimellitic acid anhydride, 2-sulfo-benzoic acid anhydride, 2-sulfo succinic acid anhydride, phthalic acid anhydride p-(O-phosphate), phthaloylchloride, succinic acid dimethyl ester, phosphorous penta chloride, phosphorous trichloride, phosphorous oxychloride, sulfonyl chloride, thionyl chloride, phosphor thionyl chloride, boric acid anhydride and boron trichloride.

31. The epoxide macromonomer of claim 24 wherein at least one E is a salt selected from the group consisting of ammonium, sulfonium, sodium, potassium, strontium, calcium and magnesium salts.

32. The macromonomer of claim 25 wherein said esterification is carried out in a solvent selected from the group consisting of THF, triethylenglycol bismethacrylate, diethylenglycol bismethacrylate, dioxolan bismethacrylate, vinyl-, vinylen- or vinyliden-, acrylate- or methacrylate substituted spiro-

orthoester, spiroorthocarbonate or bicycloorthoester and 2,2-Bis[p-(acryloxyethoxy)phenyl]propane.

33. The macromonomer of claim 25 wherein said esterification is carried out in the presence of a tertiary amine.

34. The macromonomer of claim 25 further comprising a filler, a polymerizable monomer having at least one phosphorous ester group, a polymerization initiator and a stabilizer.

35. The composition according to claim 34 further comprising a polymerizable monomer selected from the group consisting of mono- and polyfunctional (meth)-acrylate, a urethane di- and poly(meth) acrylate, a vinyl-, vinylen- or vinyliden-, acrylate- or methacrylate substituted spiro-orthoester, a spiroorthocarbonate or a bicycloorthoester, and said monomer comprises from about 5 to about 80 percent by weight.

36. The composition according to claim 34 wherein said polymerization initiator is a thermal initiator, a redox-initiator or a photoinitiator.

37. The composition according to claim 34 wherein said filler comprises an inorganic filler and/or an organic filler.

38. The composition according to claim 37 wherein said filler is a fluoride releasing inorganic filler.

39. The composition formed by polymerizing the composition of claim 34 to form a polymeric product having an adhesion to dentine of at least 2 MPa, a fluoride release of at least 1 µg F⁻ per week and per cm² of the exposed surface of the composition, an opacity of at least C_{0,7}= 40 % and a compressive strength of at least 200 MPa.

40. The composition of claim 34 comprising
from about 5 to about 20 percent by weight of said esterified macromonomer,
from about 10 to about 25 percent by weight of a di- or poly(meth)acrylate monomer having at least one phosphorous acid ester group,
from about 20 to about 35 percent by weight of a polymerizable monomer,
from about 50 to about 65 percent by weight of a filler and polymerization initiator and stabilizers.

41. The composition of claim 34 comprising

from about 3 to about 15 percent by weight of said esterified macromonomer,

from about 5 to about 25 percent by weight of di- or poly(meth)acrylate monomer having at least one phosphorous acid ester group,

from about 7 to about 40 percent by weight of a polymerizable monomer,

from about 50 to about 85 percent by weight of a filler and polymerization initiator and stabilizers.

42. The composition of claim 34 comprising

from about 5 to about 25 percent by weight of said esterified macromonomer,

from about 10 to about 30 percent by weight of di- or poly(meth)acrylate monomer having at least one phosphorous acid ester group,

from about 20 to about 40 percent by weight of a polymerizable monomer,

from about 10 to about 50 percent by weight of a filler and polymerization initiator and stabilizers.

43. The composition of claim 34 comprising

from about 5 to about 25 percent by weight of said esterified macromonomer,

from about 5 to about 30 percent by weight of di- or poly(meth)acrylate monomer having at least one phosphorous acid ester group,
from about 10 to about 40 percent by weight of a polymerizable monomer,
from about 30 to about 90 percent by weight of a diluent and polymerization initiator and stabilizers.

44. The composition of claim 34 comprising from about 1 to about 25 percent by weight of said esterified macromonomer, di- or poly(meth) acrylate monomer having at least one phosphous acid ester group and a polymerizable monomer and polymerization initiator from about 75 to about 99 percent by weight of an organic solvent and polymerization co-initiator.

45. The composition of claim 34 wherein the number of said acid moieties is chosen such that a polymer obtained by polymerizing said monomers has an adhesive strength to dentine of at least 2 MPa.--

REMARKS

The claims correspond to the claims indicated as being allowable in the corresponding European case, and are believed to be allowable. Such action is respectfully requested.

Respectfully submitted,



DALE R. LOVERCHECK
Patent Attorney Reg. No. 28638
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Address of signer:
DENTSPLY INTERNATIONAL INC.
570 West College Avenue
York, PA 18405-0872
(717) 849-4472